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# Hydrate equilibrium data for CO<sub>2</sub>+N<sub>2</sub> system in the presence of Tetra-n-butylammonium fluoride (TBAF) and mixture of TBAF and cyclopentane (CP)

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## Abstract

Hydrates can be used for CO<sub>2</sub> capture from flue gases (hydrate crystallization). In this work hydrate equilibrium data were measured and compared with literature data. The isochoric method was used to determine the gas hydrate dissociation points. Different CO<sub>2</sub>+N<sub>2</sub> gas mixtures were used with presence of promoters such as tetra-n-butylammonium fluoride (TBAF) and mixtures of TBAF and cyclopentane (CP). The key novel aspect of this work is the use of combination of promoters, TBAF and CP, which under certain conditions induced further pressure reduction in comparison to pure TBAF results. Concerning experiments with pure promoter, there is good agreement between our results and literature results for different gas mixtures and promoter concentrations.

## Introduction

The need of this work data lies in the development of novel separation methods for CO<sub>2</sub> from flue gases. There are three approaches for CO<sub>2</sub> separation: pre-combustion decarbonization, oxyfuel combustion and post combustion CO<sub>2</sub> separation. For post combustion CO<sub>2</sub> separation from flue gas, four different approaches are mainly used; chemical and physical absorption, solid physical adsorption – pressure swing and temperature swing adsorption, low temperature distillation (cryogenic separation) and membrane separation. Moreover, hydrate crystallization could become in the future an economically viable alternative process for post combustion CO<sub>2</sub> separation from flue gas in oil and gas processing<sup>1</sup>.

Gas hydrates are crystalline solids composed of water and gas. The major contrast with respect to ice is that ice forms as a pure component, while hydrates will not form without guests of the proper size. Furthermore, hydrates can form at temperatures higher than 273 K. The gas molecules (guests) are captured in water cavities (host) that consists of hydrogen-bonded water molecules. Gas molecules which typically form hydrates are methane, ethane, propane and carbon dioxide. All common natural gas hydrates belong to the three crystal structures, cubic structure I (sI), cubic structure II (sII), or hexagonal structure H (sH). In semiclathrate hydrates, the water molecules together with anions such as  $\text{Br}^-$  and  $\text{F}^-$  build a polyhedral host set of the cages in which the tetra-nbutylammonium cations ( $\text{TBA}^+$ ) are attached as guest molecules.<sup>2</sup> The main difference between semiclathrate and crystal gas hydrates, is that in the first one there are ionic interactions with the host molecules (guest molecules can both form part of the host lattice and occupy cages of the structure) while in the latter the guest molecules are not bonded physically to the host water lattices. Many studies on semiclathrate hydrates have recently reported the capture of  $\text{CO}_2$  from flue and fuel gas mixtures.<sup>3-5</sup>

Promoters (or hydrate formers) are mainly organic compounds classified in two groups: thermodynamic and kinetic. The first ones extend the hydrate formation region in a  $P$ - $T$  diagram. Kinetic promoters enhance the hydrate formation rate. Quaternary ammonium salts like tetra-nbutylammonium bromide (TBAB) and fluoride (TBAF) form ionic semiclathrate hydrates with water molecules at atmospheric pressure and they are used as thermodynamic promoters.<sup>2</sup>

From industrial point of view, the separation steps are the most costly while the design of other required equipment is in general simple.<sup>6</sup> So, the price of the promoters needed to reduce the pressure and increase the temperature is where economic studies should mainly focus on. The industry will be interested in such investments whenever the environmental regulations are rigid and when the natural gas reserves tend to reach their half-lives.

In general, for process development the operating temperature, minimum pressure for hydrate formation, the rate of hydrate formation and the separation efficiency should be established.<sup>7</sup> TBAF exhibits greater pressure reduction than TBAB.<sup>8</sup> According to literature<sup>9</sup>, the time to reach hydrate equilibrium with TBAF is about one-half of that with TBAB and one-fourth of that with THF. TBAF space velocity and  $\text{CO}_2$  separation factor are also higher than TBAB's. In addition, the highest stabilization

effect was observed at the stoichiometric concentration of pure TBAF semiclathrate, which is 3.3 mol %.<sup>10</sup> In the contrary, the gas uptake is higher for TBAB than for TBAF.<sup>11</sup>

Cyclopentane is already used as promoter in many studies.<sup>12-15</sup> Cyclopentane emulsion is formed at higher than 8.99 mol %<sup>12</sup> concentrations. The emulsion lowers the promoter's pressure reduction efficiency. The cyclopentane/water emulsion has higher hydrate formation rate than that with cyclopentane because of the larger gas and liquid contact area that controls hydrate formation rate<sup>16</sup>. In addition, the CO<sub>2</sub> selectivity in hydrates using cyclopentane is improved in comparison to the system without promoter and the equilibrium pressure is drastically reduced. However, the gas storage capacity is also reduced<sup>11</sup>. Even though cyclopentane is a very good promoter, but it stabilizes the cavities in such a way that it prevents the complete occupation of the remaining cavities by gas molecules.

In this study hydrate equilibrium results of thermodynamic promoters (TBAF and TBAF+CP) are presented and compared with existing literature. The purpose of this study is the generation of data for gas mixtures of CO<sub>2</sub> and N<sub>2</sub> with low CO<sub>2</sub> content –which simulates flue gas composition of post combustion power plant– as well as the examination whether CP induces promotion effect together with TBAF for CO<sub>2</sub>+N<sub>2</sub> gas mixtures. A preliminary literature study showed lack of data concerning this system.

## Experimental

### Experimental section

**Materials.** The chemicals used are shown in Table 1. The gas cylinders of CO<sub>2</sub> and N<sub>2</sub> gases used in this work were supplied by Air Liquide. The molar fractions of CO<sub>2</sub> in N<sub>2</sub> was 0.48 mol % which is a low CO<sub>2</sub> concentration used for oil and gas processing<sup>16</sup>. TBAF solutions with mass fractions of 0.032, 0.05 and 0.10 were prepared by the gravimetric method using an accurate analytical balance (Mettler, AT200), with mass accuracy of  $\pm 0.0001$  g. Double-distilled and deionized water from Direct-Q5 Ultrapure Water Systems (MilliporeTM), was used in all experiments. Cyclopentane at concentration of 5 vol. % was added after in 5 mol % and 10 mol % TBAF solutions with use of proper syringe.

**Table 1. Chemicals used in this study**

Chemical Name	Abbreviation	CAS-number	Purity	Phase	Supplier
Carbon dioxide	CO <sub>2</sub>	124-38-9	99.998 (Vol. %)	gas	Air Liquide
Nitrogen CO-free	N <sub>2</sub>	7727-37-9	99.999 (Vol. %)	gas	Air Liquide
Tetra-n-butylammonium fluoride	TBAF	429-41-4	75 (wt) % in H <sub>2</sub> O	liquid	Sigma Aldrich
Cyclopentane	CP	287-92-3	≥98 % (wt %)	liquid	Acros Organics
Water	H <sub>2</sub> O	7732-18-5	deionised	liquid	-

**Apparatus.** The equipment is identical to the one used in previous study<sup>17</sup>. Isochoric temperature trace method is applied. Two gas cylinders were used, one for nitrogen and one for CO<sub>2</sub> and N<sub>2</sub>. The nitrogen cylinder is used for cleaning the equilibrium cell and the CO<sub>2</sub> and N<sub>2</sub> gas cylinder contains the gas mixture of this study. The equilibrium cell is immersed in a water bath for controlling the temperature. The equilibrium cell temperature is controlled using a thermostatic water bath (LAUDA PROLine RP3530). Two platinum temperature probes (Pt100, JM6081) inserted in the cell interior –at the top (gas phase) and the bottom (liquid phase)– were used to measure the temperature inside the equilibrium cell. The temperature accuracy, determined by calibration of the respective transducers, is estimated to be ±0.02 K after careful calibration against reference platinum probe (TINSLEY Precision Instruments). The pressure in equilibrium cell is measured using a UNIK 5000 GE absolute pressure transducer with an accuracy of ±0.0015 MPa after careful calibration against dead weigh balance. The standard uncertainty of gas mixture composition  $y$  for CO<sub>2</sub>/N<sub>2</sub> (0.48/99.52) gas mixture, measured from Gas Chromatograph, for CO<sub>2</sub> is 0.58 % and for N<sub>2</sub> 0.70 %.

The equilibrium cell is made of the 316 stainless steel; its maximum working pressure and its inner volume is 40 MPa and 125 mL, respectively. A motor-driven turbine agitation system (Top Industrie, France) enables to stir the cell contents at a speed up to 1200 rpm to increase the fluids contact and enhance water conversion into hydrate. The data acquisition units (Agilent 34970A, HP 34970A) were connected

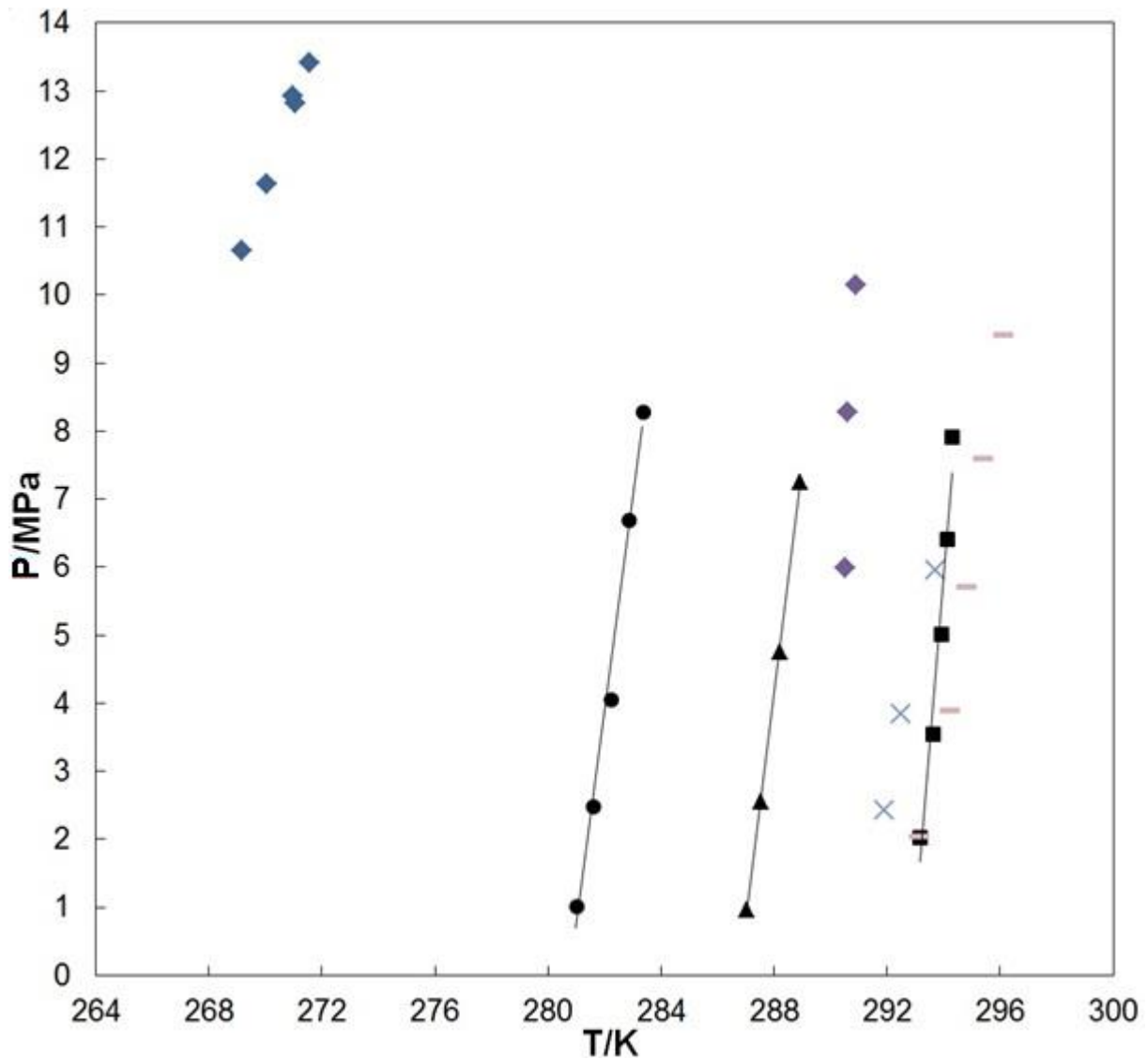
with a personal computer. Continuous recording of pressures and temperatures allows detecting any subtle changes in the system and true equilibrium conditions.

**Experimental procedure.** The procedure is similar to the one used in previous study<sup>17</sup>. After evacuation of the equilibrium cell using the vacuum pump (Oerlikon leybold vacuum, Trivac D2.5E), 25-40 ml of promoter solution (TBAF, TBAF+CP) –that is about 25-30 vol. % of the equilibrium cell– was subsequently partially filled in the equilibrium cell. Then, the gas mixture was introduced in the equilibrium cell from the cylinder. In the end, several  $P$ - $T$  equilibrium data were obtained from each experimental run and eventually a  $P$ - $T$  diagram is created following temperature-pressure trace method.

## Results and discussion

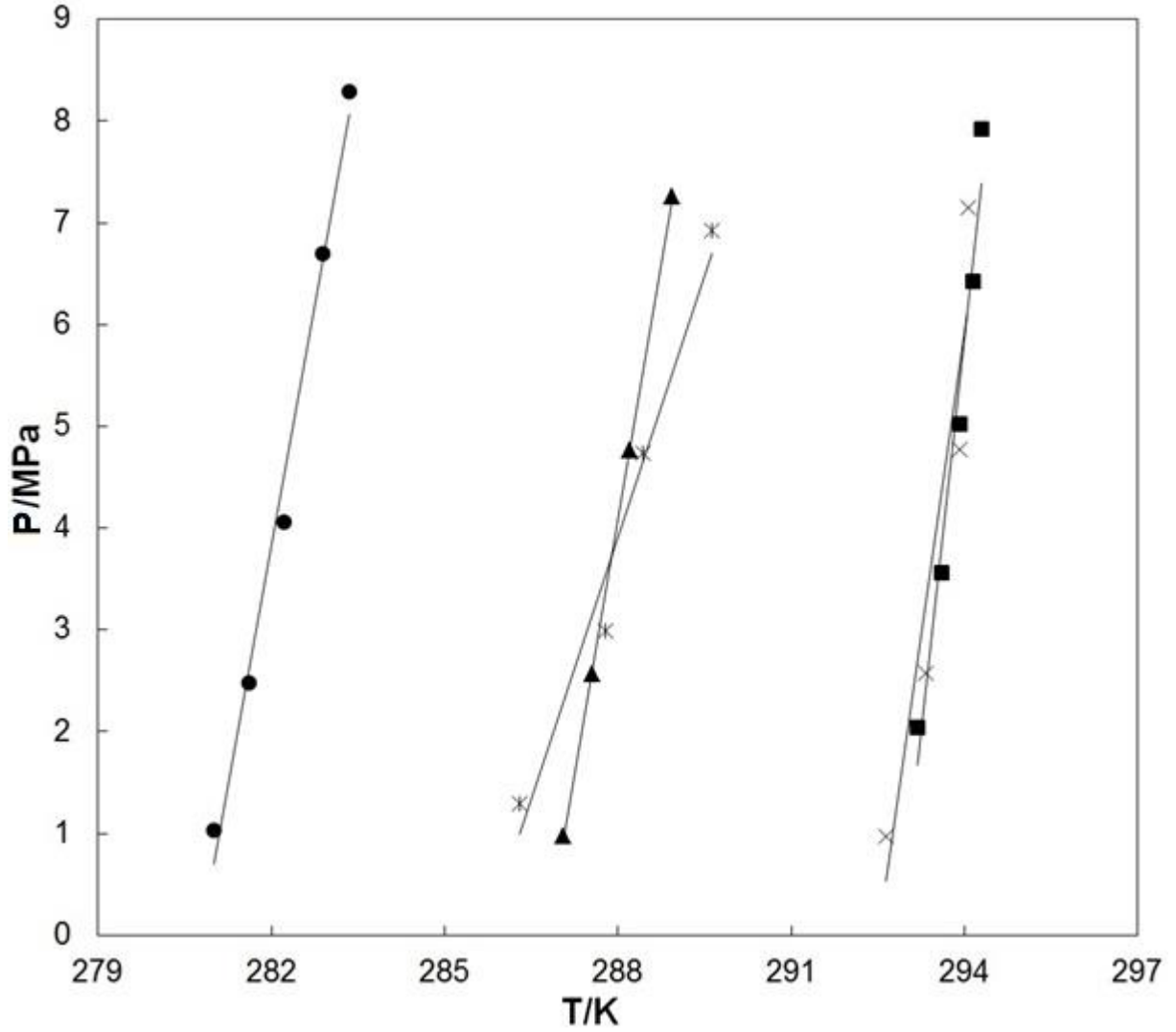
The TBAF results for  $\text{CO}_2+\text{N}_2$  gas mixture global concentrations are summarized in Figure 1. The results are compared with literature data. At first, for comparison purposes, the unpromoted system  $\text{N}_2$  is reported<sup>18</sup>. In general, it is observed good agreement of our results with the literature data for similar systems of 5% and 10 wt % TBAF solutions which correspond to 0.36% and 0.76 mol % respectively. For 3 wt % TBAF solution there are no systems in literature.

For clarity reasons, the systems are presented by two numbers in brackets. The first number denotes the mol fraction of  $\text{CO}_2$  in  $\text{CO}_2+\text{N}_2$  gas mixture cylinder and the second one denotes the promoter concentration expressed in mol %. Black markers connected with trendlines correspond to results of this work. From Gibbs phase rule, the parameters that suggest where the equilibrium lines should be located are the gas mixture concentration, the promoter concentration in aqueous solution and the water-to-gas ratio (mol/mol). For simplicity reasons and also owing to the fact that gas-to-liquid ratio is not always mentioned in literature, it was omitted from this study. The results for 3.2%, 5% and 10 wt % TBAF, which correspond to  $x=0.23\%$ ,  $x=0.36\%$  and  $x=0.76$  mol % respectively, seem well placed in the Figure 1. The gas mixture, which is 99.52% mol  $\text{N}_2$ , produced steeper results than with higher  $\text{CO}_2$  concentration. In addition 0.36 mol % TBAF are in good agreement with similar solutions from literature<sup>19-21</sup> even though the last correspond to pure  $\text{CO}_2$  results.



**Figure 1.** Hydrate dissociation points for different systems using TBAF as promoter with CO<sub>2</sub> (1) + N<sub>2</sub> (2) (0.48/99.52) gas mixture. All values are expressed in mol %. Black straight line connects the results of this work. Symbols correspond to experimental data: ◆,  $x_1=0.0$ ,  $x_{\text{TBAF}}=0.0$ , ref. 18; ●,  $x_1=0.48$ ,  $x_{\text{TBAF}}=0.23$ , this work; ▲,  $x_1=0.48$ ,  $x_{\text{TBAF}}=0.36$ , this work; ◆,  $x_1=0.0$ ,  $x_{\text{TBAF}}=0.36$ , ref. 19; ×,  $x_1=30$ ,  $x_{\text{TBAF}}=0.68$ , ref. 20; ■,  $x_1=0.48$ ,  $x_{\text{TBAF}}=0.76$ , this work; —,  $x_1=0.0$ ,  $x_{\text{TBAF}}=0.76$ , ref. 21.

Finally in Figure 2 all hydrate dissociation points of this work are presented. The use of CP for 0.76 mol % TBAF has no effect in the results while for 0.36 mol % TBAF the behavior is mixed. For low pressures (<30 bar), inhibition effect is observed while for higher pressures (>30 bar) promotion effect appears. An explanation for this behavior could be that at low pressures CP acts as inhibitor, due to its water insolubility, obstructing the hydrate formation. At higher pressures, the kinetic phenomena play more important role, so CP contributes positively to the construction of hydrates.



**Figure 2.** Hydrate dissociation points for different systems using TBAF (1) and CP (2) as promoter with CO<sub>2</sub> + N<sub>2</sub> (0.48/99.52) gas mixture. CP concentration is given in volume fraction. All other values are expressed in mol %. Black straight line connects the results of this work. Symbols correspond to experimental data: ●:  $x_1=0.23$ ,  $x_2=0.0$ , this work; ✱:  $x_1=0.36$ ,  $x_2=0.05$ , this work; ▲:  $x_1=0.36$ ,  $x_2=0.0$ , this work; ■:  $x_1=0.76$ ,  $x_2=0.05$ , this work; X:  $x_1=0.76$ ,  $x_2=0.0$ , this work.

## Consistency of experimental results

For data treatment, Clausius–Clapeyron method is applied, eq. 1. Clausius–Clapeyron equation estimates the vapor pressures of liquids or solids.

$$\frac{d\ln(P)}{d(\frac{1}{T})} = \frac{-\Delta H_{dis}}{Z \cdot R} \quad (1)$$

where  $\Delta H_{dis}$  is the apparent dissociation enthalpy of the hydrate phase,  $Z$  is the compressibility factor and  $R$  is the gas constant. Lee-Kesler-Plöcker (LKP) Equation of State (EoS)<sup>22</sup> is applied for estimation of  $Z$  as a function of  $T$  and  $P$  using binary



interaction parameter  $\kappa_{ij}=1.11$ . It is assumed very low solubility of the gas in the liquid and, thus, no changes in the gas composition.

In this study, the interest lies on the fact that for small changes of dissociation temperature, the Clausius–Clapeyron equation should predict identical (or similar)  $\Delta H_{dis}$  values. The  $\Delta H_{diss.}$  as a function of dissociation temperature shows the goodness of fit (which is shown by the Coefficient of determination ( $R^2$ )). Coefficient of determination ( $R^2$ ) is used to show how well fit the  $\Delta H$  values (kJ/mol) in the straight line of  $\Delta H(T)$ . Table 2 presents the data treatment for TBAF results of this work and from literature.

**Table 2. Coefficient of determination ( $R^2$ ) of  $\Delta H_{diss.}$  (kJ/mol) in terms of temperature including TBAF literature**

Promoter concentration (mol %)	CO <sub>2</sub> global concentration of feed in CO <sub>2</sub> +N <sub>2</sub> gas mixture (mol %)	Coefficient of determination ( $R^2$ )	Literature
<u>TBAF+CP</u>			
0.36	0.05	0.995	this work
0.76	0.05	0.864	this work
<u>TBAF</u>			
0.23	0.05	0.997	this work
0.36	0.05	0.991	this work
0.76	0.05	0.993	this work
0.29	100	0.285	Li et al. <sup>23</sup>
0.62	100	0.984	Li et al. <sup>23</sup>
0.14	100	0.986	Mohammadi et al. <sup>19</sup>
0.36	100	0.935	Mohammadi et al. <sup>19</sup>
1.20	100	0.734	Mohammadi et al. <sup>19</sup>
0.80	100	0.985	Lee et al. <sup>10</sup>
3.00	100	0.938	Lee et al. <sup>10</sup>
3.30	100	0.958	Lee et al. <sup>10</sup>
5.30	100	0.926	Lee et al. <sup>10</sup>
0.36	30.0	0.997	Sfaxi et al. <sup>20</sup>
0.68	30.0	0.988	Sfaxi et al. <sup>20</sup>
0.00	0.0	0.928	Van Cleeff and Diepen <sup>18</sup>
0.36	0.0	0.841	Mohammadi et al. <sup>19</sup>
1.20	0.0	0.922	Mohammadi et al. <sup>19</sup>
0.76	0.0	0.504	Lee et al. <sup>21</sup>
1.69	0.0	0.627	Lee et al. <sup>21</sup>
3.43	0.0	0.812	Lee et al. <sup>21</sup>
5.33	0.0	0.588	Lee et al. <sup>21</sup>

The results of this work are very good ( $R^2>0.90$ ) except for the system of 0.72 mol % of TBAF+CP mixture. The system of 0.29 mol % in pure CO<sub>2</sub> gas of Li et al.<sup>23</sup> and 1.2 mol % in pure CO<sub>2</sub> gas, 0.36 mol % in pure N<sub>2</sub> gas of Mohammadi et al.<sup>19</sup> as well as

the systems of Lee et al.<sup>21</sup> are problematic ( $R^2 < 0.90$ ). The rest systems from literature seem to be very good.

## Experimental Uncertainties

The experimental uncertainties are presented in Tables 3 and 4. The standard temperature and pressure uncertainties are proved to be satisfactory.

**Table 3. Hydrate equilibrium point for TBAF solution with standard temperature and pressure uncertainties,  $U(T)$  and  $U(P)$ .**

T/K	P/MPa	TBAF concentration/ wt % (mol %)	U (T)/K	U(P)/MPa
293.18	2.03	10 (0.76%)	0.057	0.0021
293.61	3.55	10 (0.76%)	0.035	0.0019
293.91	5.01	10 (0.76%)	0.030	0.0019
294.14	6.42	10 (0.76%)	0.025	0.0018
294.30	7.91	10 (0.76%)	0.049	0.0029
287.05	0.97	5 (0.36%)	0.023	0.0017
287.55	2.55	5 (0.36%)	0.023	0.0017
288.20	4.76	5 (0.36%)	0.033	0.0018
288.93	7.25	5 (0.36%)	0.028	0.0019
280.99	1.02	3.2 (0.23%)	0.023	0.0017
281.61	2.48	3.2 (0.23%)	0.023	0.0017
282.23	4.05	3.2 (0.23%)	0.023	0.0017
282.88	6.69	3.2 (0.23%)	0.023	0.0017
TBAF – wt% (mol %) +5 vol. % CP				
292.64	0.97	10 (0.76%)	0.023	0.0017
293.34	2.57	10 (0.76%)	0.023	0.0017
293.91	4.77	10 (0.76%)	0.023	0.0017
294.05	7.14	10 (0.76%)	0.023	0.0017
286.29	1.28	5 (0.36%)	0.023	0.0017
287.78	2.99	5 (0.36%)	0.023	0.0017
288.44	4.73	5 (0.36%)	0.023	0.0017
289.62	6.91	5 (0.36%)	0.023	0.0017

Gas mixture composition standard uncertainty for  $\text{CO}_2/\text{N}_2$  (0.48/99.52) gas mixture is  $U(y\text{CO}_2) = 0.58 \%$  and  $U(y\text{N}_2) = 0.70 \%$ .

**Table 4. Gas molar composition and gas inserted in equilibrium cell standard uncertainty  $U(n_{\text{gas}})$  for every hydrate equilibrium point**

$\text{CO}_2$ inserted/	$\text{N}_2$ inserted/	$\text{H}_2\text{O}$ inserted/	Promoter inserted/	$U(n_{\text{gas}})/\%$	Promoter concentration/ wt %
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mol	mol	mol	mol			
0.000199	0.0647	1.74	0.01276	1.94	10%	TBAF
0.000218	0.0711	1.74	0.01276	1.85	10%	TBAF
0.000225	0.0732	1.74	0.01276	1.83	10%	TBAF
0.000231	0.0753	1.74	0.01276	1.80	10%	TBAF
0.000397	0.1293	1.74	0.01276	1.78	10%	TBAF
0.000419	0.1364	1.94	0.00674	1.67	5%	TBAF
0.000227	0.0739	1.94	0.00674	2.02	5%	TBAF
0.000316	0.1030	1.94	0.00674	1.72	5%	TBAF
0.000318	0.1037	1.94	0.00674	1.72	5%	TBAF
0.000111	0.0362	2.03	0.03318	2.25	3.2%	TBAF
0.000181	0.0590	2.03	0.03318	1.76	3.2%	TBAF
0.000177	0.0576	2.03	0.03318	2.72	3.2%	TBAF
0.000384	0.1251	2.03	0.03318	1.99	3.2%	TBAF
0.000161	0.0526	2.03	0.03318	2.90	3.2%	TBAF
0.000212	0.0689	1.26	0.02430	1.82	10%	TBAF+CP (5 vol. %)
0.000216	0.0703	1.26	0.02430	1.81	10%	TBAF+CP (5 vol. %)
0.000382	0.1243	1.26	0.02430	1.77	10%	TBAF+CP (5 vol. %)
0.000456	0.1485	1.26	0.02430	1.73	10%	TBAF+CP (5 vol. %)
0.000157	0.0512	1.31	0.01902	1.96	5%	TBAF+CP (5 vol. %)
0.000297	0.0966	1.31	0.01902	1.72	5%	TBAF+CP (5 vol. %)
0.000268	0.0874	1.31	0.01902	1.74	5%	TBAF+CP (5 vol. %)
0.000395	0.1286	1.31	0.01902	1.68	5%	TBAF+CP (5 vol. %)

## Conclusions

Hydrate equilibrium points for CO<sub>2</sub> and N<sub>2</sub> were measured with the use of tetra-n-butylammonium bromide (TBAF) and mixture of TBAF with CP as promoters. The use of TBAF concentration (0.36 mol %) and CP (5 vol. %) revealed promotion effect at pressures higher than 3.5 MPa. On the contrary, the results have shown that the simultaneous use of TBAF (0.76 mol %) with CP (5 vol. %) did not have any impact on thermodynamic equilibrium. The equilibrium results are more dependent on TBAF concentration rather than gas mixture concentration as the comparison with literature data revealed. The consistency analysis has shown that the results of this study are satisfactory.

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## Notes

The authors declare no competing financial interest.

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## References

- (1) Todd, A.C., CCS—A multidisciplinary global activity for a global challenge, *Chem. Eng. Res. Des.* **2011**, 89, 1443-1445.
- (2) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-n-butylammonium bromide-water (1/38). *Acta Crystallogr.* **2005**, C61, o65–o66.
- (3) Li, X. S.; Xia, Z. M.; Chen, Z. Y.; Wu, H. J. Precombustion capture of carbon dioxide and hydrogen with a one-stage hydrate/membrane process in the presence of tetra-n-butylammonium bromide (TBAB). *Energy Fuels* **2011**, 25, 1302–1309.
- (4) Kim, S. M.; Lee, J. D.; Lee, H. J.; Lee, E. K.; Kim, Y. Gas hydrate formation method to capture the carbon dioxide for pre-combustion process in IGCC plant. *Int. J. Hydrogen Energ.* **2011**, 36, 1115–1121.
- (5) Belandria, V.; Mohammadi, A. H.; Eslamimanesh, A.; Richon, D.; Sánchez-Mora, M. F.; Galicia-Luna, L. A. Phase equilibrium measurements for semi-clathrate hydrates of the (CO<sub>2</sub> + N<sub>2</sub> + tetra-nbutylammonium bromide) aqueous solution systems: Part II. *Fluid Phase Equilib.* **2012**, 322–323, 105–112.
- (6) Feron, P. H. M.; Hendriks, C. A. CO<sub>2</sub> capture process principles and costs. *Oil Gas Sci. Techn.* **2005**, 60, 451-459.

- (7) Linga, P.; Kumar, R.; Englezos, P. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J. Hazard. Mater.* **2007**, *149*, 625-629.
- (8) Li, S.; Fan, S.; Wang, J.; Lang, X.; Wang, Y. Semiclathrate Hydrate Phase Equilibria for CO<sub>2</sub> in the Presence of Tetra-n-butyl Ammonium Halide (Bromide, Chloride, or Fluoride). *J. Chem. Eng. Data* **2010**, *55*, 3212–3215.
- (9) Fan, S.; Li, S.; Wang, J.; Lang, X.; Wang, Y. Efficient Capture of CO<sub>2</sub> from Simulated Flue Gas by Formation of TBAB or TBAF Semiclathrate Hydrates. *Energy Fuels* **2009**, *23*, 4202–4208.
- (10) Lee, S.; Lee, Y.; Park, S.; Kim, Y.; Lee J.-D.; Seo, Y. Thermodynamic and Spectroscopic Identification of Guest Gas Enclathration in the Double Tetra-n-butylammonium Fluoride Semiclathrates. *J. Phys. Chem. B* **2012**, *116*, 9075–9081.
- (11) Park, S.; Lee, S.; Lee, Y.; Seo, Y. CO<sub>2</sub> Capture from Simulated Fuel Gas Mixtures Using Semiclathrate Hydrates Formed by Quaternary Ammonium Salts. *Environ. Sci. Technol.* **2013**, *47*, 7571–7577.
- (12) Galfré, A.; Kwaterski, M.; Brântuas, P.; Cameirao, A.; Herri, J.-M., Clathrate Hydrate Equilibrium Data for the Gas Mixture of Carbon Dioxide and Nitrogen in the Presence of an Emulsion of Cyclopentane in Water. *J. Chem. Eng. Data* **2014**, *59*, 592–602.
- (13) Zhang, J.; Lee, J.W. Enhanced Kinetics of CO<sub>2</sub> Hydrate Formation under Static Conditions. *J. Chem. Eng. Data* **2009**, *54*, 659–661.
- (14) Mohammadi, A.; Richon, D. Phase equilibria of binary clathrate hydrates of nitrogen + cyclopentane/cyclohexane/methylcyclohexane and ethane + cyclopentane/cyclohexane/methyl cyclohexane. *Chemical Engineering Science* **2011**, *66*, 4936–4940.
- (15) Herslund, P.J.; Thomsen, K.; Abildskov, J.; von Solms, N.; Galfré, A.; Brântuas, P.; Kwaterski, M.; Herri, J.-M. Thermodynamic Promotion of Carbon Dioxide Clathrate Hydrate Formation by Tetrahydrofuran, Cyclopentane and their Mixtures. *Int. J. of Greenh. Gas Control* **2013**, *17*, 397–410.
- (16) Chen, C.; Li, X.-S.; Chen, Z.-Y.; Xia, Z.-M.; Yan, K.-F.; Cai, J. Equilibrium Hydrate Formation Conditions of CO<sub>2</sub>+N<sub>2</sub>+SO<sub>2</sub> Ternary Simulated Flue Gas in SO<sub>2</sub> and Tetra-n-butylammonium Bromide Containing Aqueous Solutions. *J. Chem. Eng. Data* **2014**, *59*, 103–109.
- (17) Tzirakis, F.; Stringari, P.; von Solms, N.; Coquelet, C.; Kontogeorgis, G. Hydrate equilibrium data for the CO<sub>2</sub>+N<sub>2</sub> system with the use of Tetra-n-butylammonium bromide (TBAB), cyclopentane (CP) and their mixture. *Fluid Phase Equilib.* **2016**, *408*, 240-247.
- (18) Van Cleeff, A.; Diepen, G. A. M. Gas Hydrates of Nitrogen and Oxygen. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 582–586.
- (19) Mohammadi, A.; Manteghian, M.; Mohammadi, A. H. Dissociation Data of Semiclathrate Hydrates for the Systems of Tetra-n-butylammonium Fluoride (TBAF) + Methane + Water, TBAF + Carbon Dioxide + Water and TBAF + Nitrogen + Water. *J. Chem. Eng. Data* **2013**, *58*, 3545–3550.
- (20) Sfaxi, I.; Durand, I.; Lugo, R.; Mohammadi, A.; Richon, D. Hydrate phase equilibria of CO<sub>2</sub>+N<sub>2</sub>+aqueous solution of THF, TBAB or TBAF system. *Int. J. of Greenh. Gas Control* **2014**, *26*, 185–192.
- (21) Lee, S.; Lee, Y.; Park, S.; Seo, Y. Phase Equilibria of Semiclathrate Hydrate for Nitrogen in the Presence of Tetra-n-butylammonium Bromide and Fluoride. *J. Chem. Eng. Data* **2010**, *55*, 5883–5886.

- (22) Plöcker, U.; Knapp, H.; Prausnitz, J. M. Calculation of High-Pressure Vapor-Liquid Equilibria from a Corresponding-States Correlation with Emphasis on Asymmetric Mixtures. *Int. Chem. Proc.* **1978**, *17*, 324-334.
- (23) Li, S.; Fan, S.; Wang, J.; Lang, X.; Wang, Y. Semiclathrate Hydrate Phase Equilibria for CO<sub>2</sub> in the Presence of Tetra-*n*-butyl Ammonium Halide (Bromide, Chloride, or Fluoride), *J. Chem. Eng. Data* **2010**, *55*, 3212–3215.